

FINAL TECHNICAL REPORT

PROPERTIES OF COPOLYMER-CONTAINING BLENDS:  
THE ROLE OF MOLECULAR ARCHITECTURE

GRANT AFOSR F49620-96-1-0108

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- II. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz  
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- III. GRANT NUMBER: AFOSR F49620-96-1-0108
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## VI. ABSTRACT OF ACCOMPLISHMENTS

Several investigations concerning the synthesis, structure and properties of polyphenylene vinylene (PPV) and related macromolecules with novel electro-optical characteristics have been completed. Selected homopolymers and copolymers of systematically varying architecture have been designed and synthesized and shown to be highly efficient chromophores in electroluminescent devices. Several of these polymers have also been shown to be efficient lasing materials in optically-pumped configurations. The study of the phase behavior of polymer blends has continued with emphasis on sequence distribution effects in the respective copolymer constituent(s). Dynamic light scattering studies of solvated flexible polymer chains have probed the coil-globule transition below the  $\theta$ -point and related this to current theory. Other studies have investigated the properties of polyvinyl butyral blends, the detailed structure of doped polyphenylene vinylene and other conducting polymers, and the photophysics of stilbene derivatives.

## VII. DESCRIPTION OF RESEARCH UNDERTAKEN

The grant has supported several lines of research in the physical chemistry of macromolecules, including some that have continued from earlier AFOSR funding.

The results have in large part been published (48 papers, published and in press) in the open literature, and representative highlights are discussed below.

A. Electro-optically Active Polymers (5, 7, 9, 12, 13, 14, 15, 16, 18, 20, 23, 24, 26, 27, 30, 33, 39, 41, 42, 45, 46, 47, 48<sup>1</sup>)

We have pursued our integrated research program in this area in which novel polymers have been a) synthesized (b characterized, especially with respect to their photo-physically properties and c) fabricated into devices such as light emitting diodes and optically-pumped lasers. Examples are given below.

### a) Synthesis

A variety of novel light emitting polymers based on poly(*p*-phenylene vinylene) containing alternating conjugated and non-conjugated blocks have been prepared using the Wittig condensation reaction. Different electron donating and withdrawing groups, as well as various aromatic and heterocyclic rings, were incorporated into the structure, and all polymers were soluble in standard organic solvents. Photoluminescence and electroluminescence emission from single layer LEDs fabricated from these materials ranged from the blue ( $\lambda_{\text{MAX}} 445 \text{ nm}$ ) to the orange ( $\lambda_{\text{MAX}} 591 \text{ nm}$ ) regions of the UV/Visible

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<sup>1</sup>The numbers in this section headings correspond to the publications listed in Section VIII.



spectrum, with several exhibiting excellent luminescence characteristics.

The attractiveness of using organic  $\pi$ -conjugated polymers over inorganic materials in light emitting diodes (LEDs) has been apparent since the discovery of the first light emitting polymer, poly(*p*-phenylene vinylene) (PPV). These polymeric light emitting materials have significant potential in future electronic devices due to their inherent flexibility and ease of processing, coupled with their useful electronic properties. To date, many have been prepared based on the fully conjugated PPV structure.

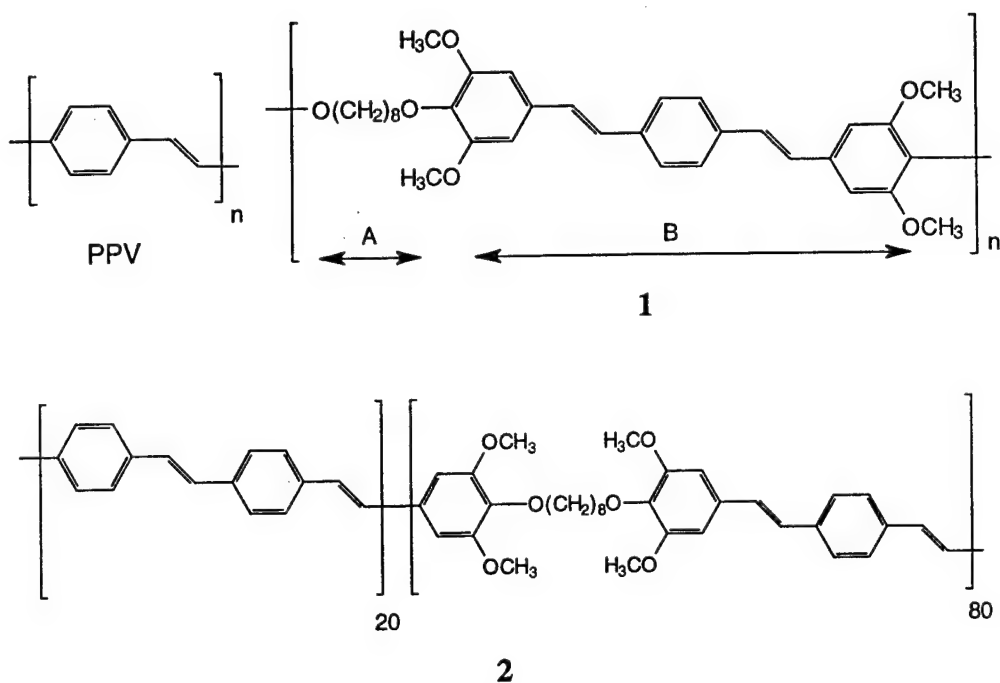
The photoluminescent (PL) and electroluminescent (EL) properties of copolymers containing alternating conjugated and non-conjugated blocks have been studied here and compared to those in fully conjugated polymers. These copolymers offer a convenient way to tailor the molecular design for specific purposes, while decreasing crystallinity and improving the solubility in organic solvents, which in turn facilitates improved processibility and film formation. Confining the  $\pi$ -conjugation to shorter segments, which often results in blue-shifting of the EL emission, leads to higher luminescent efficiency when compared to polymers with regular conjugation. In the PPV system, when random interruption of the conjugation occurred, it was demonstrated that the quantum efficiency was increased by up to two orders of magnitude.

Utilization of the alternating block copolymer concept with an oligomethylene spacer and a phenylene vinylene (PV) chromophore has been studied previously by our group using copolymers prepared by means of a

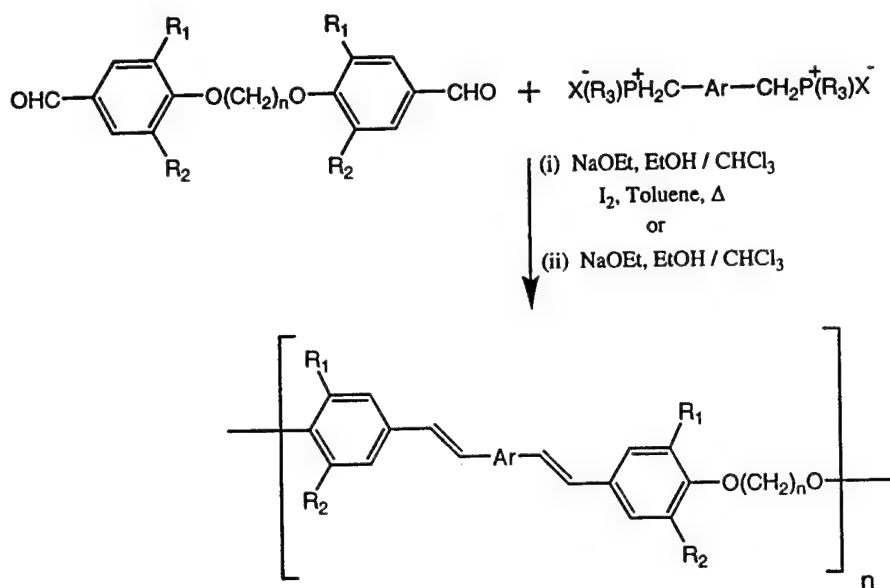
Wittig condensation reaction. This step-growth polycondensation reaction involves coupling of aromatic dialdehydes with phosphonium salt monomeric precursors to form the vinylic double bond in the resultant polymer. The step-growth polymerization also allows good experimental control of copolymer formation, and changes in the copolymer structure can be simply effected by use of two or more different monomeric precursors in the polymerization mix.




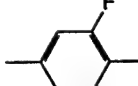
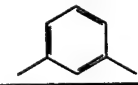

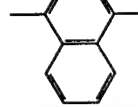
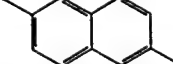
Work in this area has concentrated on varying the lengths of the alternating conjugated/non-conjugated blocks. This study focuses on the effect that molecular architecture changes have on the overall light emitting properties of the chromophoric systems shown in Figure 1. Changes in structure include the addition of electron donating or withdrawing groups, as well as inclusion of different aromatic and heterocyclic rings in the chromophore/s (Schemes 1, 2 and 3).

To prepare a polymer with improved blue electroluminescence, it was known that replacing the methoxy groups on copolymer 1 with methyl groups would cause blue-shifting of the EL, due to reduced electron density of the conjugated  $\pi$ -system induced by the methyl groups when compared to the methoxy groups, a phenomenon which has been previously observed. Thus, copolymer 3 was synthesized and while its PL spectrum showed two peaks of equal intensity in the blue region ( $\lambda_{\text{MAX}}$  447 nm and 465 nm), low solubility of the material in organic solvents contributed to poor EL spectra being recorded. A more soluble derivative was prepared by extending the alkyloxy chain from



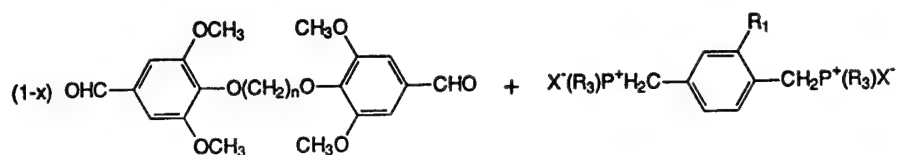
**Figure 1** Structural representations of PPV, the alternating block copolymer **1** with a non-conjugated oligomethylene segment (A) and a conjugated '2½' phenylene vinylene (PV) segment (B), and the modified PV copolymer **2** with an additional dimeric PV unit incorporated into the structure.<sup>10-12</sup>



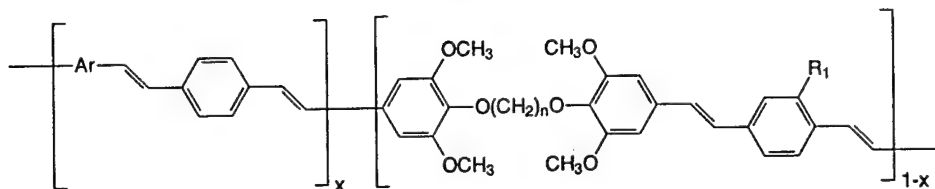
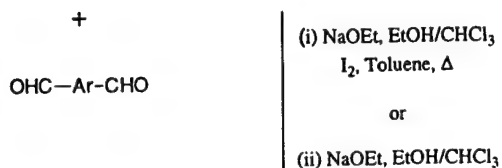
Compd. #	Ar	n	R <sub>1</sub>	R <sub>2</sub>	<sup>†</sup> R	T <sub>g</sub> (°C)	M <sub>w</sub> (10 <sup>3</sup> )
3		8	CH <sub>3</sub>	CH <sub>3</sub>	Ph	67	17.2
4		12	CH <sub>3</sub>	CH <sub>3</sub>	Bu	64	13.4
5		8	OCH <sub>3</sub>	Br	Bu	62	40.9
6		8	OCH <sub>3</sub>	OCH <sub>3</sub>	Ph	85	23.9
7		8	OCH <sub>3</sub>	OCH <sub>3</sub>	Ph	62	18.5
8		8	OCH <sub>3</sub>	OCH <sub>3</sub>	Bu	--	2.8
9		8	OCH <sub>3</sub>	OCH <sub>3</sub>	Bu	--	11.2
10		8	OCH <sub>3</sub>	OCH <sub>3</sub>	Bu	--	2.7



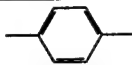
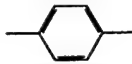

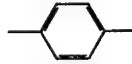
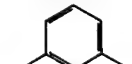
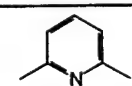
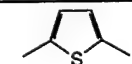

<sup>†</sup>Polymers prepared using Bu<sub>3</sub> salt were not fully isomerized using I<sub>2</sub> and were ≥ 90% *trans* (<sup>1</sup>H nmr spectra).

Scheme 1

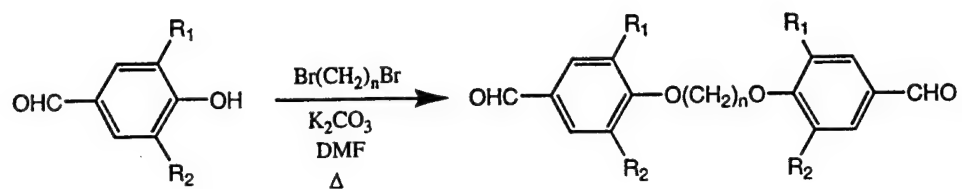


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Compd. #	Ar	x	n	R	R <sub>1</sub>	Method*	M <sub>w</sub> (10 <sup>3</sup> )	T <sub>g</sub> (°C)
11		0.1	8	PPh <sub>3</sub>	H	(i)	24.9	Not measured
2		0.2	8	PPh <sub>3</sub>	H	(i)	18.8	Not measured
12		0.4	8	PPh <sub>3</sub>	H	(i)	10.8	74
13		0.2	4	PBu <sub>3</sub>	H	(ii)	6.1	100
14		0.2	12	PBu <sub>3</sub>	H	(ii)	69.4	71
15		0.2	8	PPh <sub>3</sub>	F	(i)	23.4	80
16		0.2	8	PPh <sub>3</sub>	H	(i)	25.2	92
17		0.2	8	PBu <sub>3</sub>	H	(ii)	27.1	85
18		0.2	8	PPh <sub>3</sub>	H	(i)	19.0	75
19		0.2	8	PBu <sub>3</sub>	H	(ii)	55.7	86

Scheme 2



Comp. #	$R_1$	$R_2$	n	Yield (%)	m.p. ( $^{\circ}\text{C}$ )
20	$\text{OCH}_3$	$\text{OCH}_3$	4	40	154-156
21	$\text{OCH}_3$	$\text{OCH}_3$	8	85	87-88
22	$\text{OCH}_3$	$\text{OCH}_3$	11	70	50-52
23	$\text{OCH}_3$	$\text{OCH}_3$	12	52	80-82
24	$\text{CH}_3$	$\text{CH}_3$	8	58	93-95
25	$\text{CH}_3$	$\text{CH}_3$	12	77	89-91
26	$\text{OCH}_3$	Br	8	63	101-103

Scheme 3

8 methylene units to 12, with *ca.* 90% *trans* double bond configuration. The EL spectrum for **4** exhibited a peak ( $\lambda_{\text{MAX}}$ 468 nm) and a shoulder ( $\lambda_{\text{MAX}}$ 445 nm) in the blue region, suggesting that there is possibly more than one chromophore contribution to the electroluminescence. While changing the alkyl groups on the aromatic rings from methoxy to methyl caused some slight blue-shifting of the EL, the brightness (120 cd/m<sup>2</sup>) and EL quantum efficiency (~0.02%) for copolymer **4** was lower than that typically obtained for the blue copolymer **1**.

Introduction of an electron withdrawing group on the center ring of the conjugated segment (copolymer **6**) caused red-shifting of the luminescence when compared to **1**, resulting in blue-green photoluminescence ( $\lambda_{\text{MAX}}$ 479 nm) and green electroluminescence ( $\lambda_{\text{MAX}}$ 507 nm). The fluorine electron withdrawing group enhanced the electron dispersion within the chromophore, which led to a decrease in size of the band gap, and resulted in the red-shifted PL and EL spectra. Inclusion of a *meta*-substituted aryl ring in place of a *para*-substituted ring (copolymer **7**) resulted in slightly blue-shifted photoluminescence ( $\lambda_{\text{MAX}}$ 450 nm), but borderline blue to blue-green electroluminescence ( $\lambda_{\text{MAX}}$ 483 nm). The possibility of side-product formation in the reaction to form this copolymer explains the blue to blue-green shift in EL for this polymer, since it is expected that *meta*-substitution would lead to blue-shifted electroluminescence in this type of conjugated polymer system. Investigations have shown that partially replacing the phenylene units in PPV

with a naphthalene system linked through the 1,4- or the 2,6-positions had substantial effects. If the naphthalene units were linked via the 2,6-positions, little or no change in EL emission was observed. However, incorporation of 1,4-substituted naphthalene resulted in large red-shifting of photoluminescence and electroluminescence maxima of the copolymers. This phenomenon was attributed to the HOMO-LUMO band gap being similar for 1,4-phenylene and 2,6-naphthalene substitution, predicted from molecular orbital calculations. The same calculations showed that 1,4-naphthalene substitution resulted in a smaller band gap, thus causing the red-shift in the photoluminescence and electroluminescence.

Thus 1,4- and 2,6-substituted naphthalenes were incorporated into the copolymer **1** structure, resulting in copolymers **9** and **10** respectively. Due to the low yield of the 2,6-substituted copolymer **10**, only solid-state PL spectra were used to compare the effect of the different substitution patterns. It is evident that the PL emission of the 1,4-substituted polymer **9** is significantly red-shifted when compared to 2,6-substituted copolymer **10** [PS:  $\lambda_{\text{MAX}}$  507 nm (green) for 1,4-substitution and  $\lambda_{\text{MAX}}$  462 nm (blue) for 2,6-substitution]. This is consistent with the results described earlier. An EL spectrum was recorded for the 1,4-copolymer **9**, with a single peak emission at 511 nm (green region). This simple architectural modification to the copolymer **1** structure also provided a convenient method for synthesizing green EL copolymers from blue EL copolymers.



An interesting comparison was made between the copolymer **34** containing both methyl and methoxy groups attached to the chromophores, the blue copolymer **1** and the copolymer with only methyl substitution **4**. Solid state PL for copolymer **34** exhibited single peak emission in the blue region ( $\lambda_{\text{MAX}}$  460 nm), similar to that exhibited by copolymer **1**. While copolymers **1** and **4** exhibit blue electroluminescence, copolymer **34** emitted in the green region ( $\lambda_{\text{MAX}}$  500 nm) with a single broad maximum.

Introduction of 1,3-phenylene (*meta*) substitution in this system (copolymer **16**) caused significant blue-shifting of the PL and EL emission when compared to copolymer **2**, resulting in blue photo- and electroluminescence (PL,  $\lambda_{\text{MAX}}$  473 nm; EL,  $\lambda_{\text{MAX}}$  481 nm). This suggests that the inclusion of the 1,3-phenylene substitution pattern prevented the efficient intra- and intermolecular energy transfer from the shorter to longer conjugated segments, the opposite of what was previously observed for 1,4-phenylene substitution in copolymer **2**. This means that both PL and EL are dominated by the '2½' PV units, making up about 76% of the polymer, and which is responsible for the blue PL and EL emission. Copolymer **16** typically had lower luminescence intensity when compared to copolymer **2** and the blue copolymer **1**.

Introduction of a pyridine ring with a 2,6-substitution pattern (copolymer **17**) in place of the 1,4-phenylene ring yielded a pale yellow fibrous polymer similar to the blue copolymer **1**, and indeed exhibited blue

photoluminescence ( $\lambda_{\text{MAX}}$  472 nm) when excited at 370 nm. This suggested that the 2,6-pyridine ring had a similar effect on the conjugated system to that of the 1,3-phenylene ring (copolymer 16). However, this same polymer unexpectedly exhibited orange electroluminescence of low intensity ( $\lambda_{\text{MAX}}$  591 nm) with an unusually broad EL spectrum. This behavior has been witnessed for some *p*-phenylene ethynylene conjugated polymers, but not for the type of conjugated system used in this work. One reason for this effect is that different recombination centers dominated the PL and EL spectra due to the difference in the excitation mechanism (direct photo-induced singlet formation in the PL versus separate charge injection in EL). On application of an electric field, the 2,6-pyridine ring in copolymer 17 could also enhance the intra- and intermolecular energy transfer from the shorter conjugated segments to the longer ones, more so than for the 1,4-phenylene units in copolymer 2.

#### b) Characterization: carrier mobility

The transport characteristics of electrons and holes in an alternating block copolymer, poly(1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene), have been investigated by current-voltage measurements in metal/polymer/metal sandwich structures. Strong evidence that the hole current is space-charge limited with a single discrete set of

shallow traps and the electron current is space-charge limited with an exponential distribution of traps was obtained. A hole trap density of  $\sim 1 \times 10^{17} \text{ cm}^{-3}$  and a hole trap energy of  $\sim 0.1 \text{ eV}$  relative to the highest occupied molecular orbital level were determined. The characteristic energy of the trap distribution,  $\sim 0.05 \text{ eV}$ , and the trap density  $< 3.7 \times 10^{17} \text{ cm}^{-3}$  for electrons were also estimated. It was found that the hole current became trap-free, space-charge limited, when using Au, Pd or Ni ( $\phi_{\text{Au}} \approx \phi_{\text{Pd}} \approx \phi_{\text{Ni}} \approx 5.1 \text{ eV}$ ) instead of Cu as the anode, indicating that the hole trap energy must lie between  $\phi_{\text{Cu}}$  ( $\approx 4.65 \text{ eV}$ ) and  $\phi_{\text{Au}}$ . A hole mobility of  $\sim 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  in this copolymer was determined.

The transport characteristics of the holes in the copolymer were investigated using X/polymer/Al devices (X: Cu, Au, Pd, or Ni; Al negative bias). In Fig. 2 current voltage characteristics of a Cu/polymer/Al device are shown. It can be seen that in the increasing voltage portion of the  $I(V)$  curve three segments can be identified, corresponding to an ohmic region ( $j \propto V$ ) (a), at low voltage, which then becomes space-charge limited with a single discrete set of shallow traps ( $j \propto V^2$ ) (b), and a final trap-filled region (c) with a further increase of the voltage. These regions can be well explained using standard space-charge limited current (SCLC) theory.

Charge transport through a thin organic polymer film may be an electrode limited process or a bulk limited process. In the second case, i.e. a SCLC process, in the absence of traps in the polymer, the current density can

be written as follows:

$$j = \frac{9}{8} \epsilon \mu \frac{V^2}{d^3}$$

where  $\epsilon$  is the permittivity of the polymer,  $d$  is the polymer film thickness,  $\mu$  is the charge carrier mobility and  $V$  is the applied voltage.

If traps are present in the polymer, the SCLC may be decreased by several orders or magnitude. It has been argued that neither the space-charge density nor the field distribution

$$j = \frac{9}{8} \epsilon \mu \theta \frac{V^2}{d^3}$$

should be altered by trapping, but that the equation relating current to voltage should be modified by a trap-limiting parameter  $\theta$  relating the proportion of trapped charges ( $p_t$ ) to free charges ( $p$ ), i.e.,  $j$  is now written where  $\theta$  is given by

$$\theta = \frac{p}{p + p_t}$$

Thus for the trap free case,  $p_t = 0$ , therefore  $\theta = 1$ ; with traps present,  $\theta$  is always less than unity.

The parameters  $p$  and  $p_t$  are given by

$$p = N_v \exp\left(-\frac{E_f - E_v}{kT}\right)$$

$$p_t = \frac{N_t}{1 + \exp\left(\frac{E_f - E_t}{kT}\right)}$$

where  $N_v$  is the density of states in the valence band,  $N_t$  is the density of traps,  $E_f$  is the relevant Fermi level and  $E_t$  is the energy level of the traps;  $\kappa$  is the Boltzmann constant. Therefore, for traps lying at an energy  $E_t$  below the  $E_f$  such that  $(E_f - E_t)/\kappa T > 1$  and  $p_t > p$ ,

$$\theta = \frac{N_v}{N_t} \exp\left(-\frac{E_t - E_v}{\kappa T}\right)$$

Substituting for  $\theta$  yields

$$j = \frac{9}{8} \epsilon \mu \frac{N_v}{N_t} \exp\left(-\frac{E_t - E_v}{\kappa T}\right) \frac{V^2}{d^3}$$

This equation is referred to as Child's law for a polymer with shallow traps. Since  $\mu$  is the mobility of free carriers, and defining the effective mobility as

$$\mu_{eff} = \mu \frac{N_v}{N_t} \exp\left(-\frac{E_t - E_v}{\kappa T}\right)$$

equation may be rewritten as

$$j = \frac{9}{8} \epsilon \mu_{eff} \frac{V^2}{d^3}$$

The effective mobility  $\mu_{eff}$ , which is reduced by the presence of traps, can be obtained by fitting Eq. (8) to the experimental data. The value of  $E_t$  can thus be obtained using Eq. (7), if the temperature dependence of  $\mu_{eff}$  is also measured.

As the current increases with increasing applied voltage, the Fermi level  $E_f$  moves to energies closer to the valence band and may eventually cross the

energy level of the traps at  $E_t$ . As this point, the trap will essentially become filled and a further increase in voltage will result in the introduction of free carriers that cannot be trapped again. This will be observed experimentally as a rather sudden and large increase in the current, such as seen in region (c) shown in Fig. 2. The voltage at which this large increase in the current occurs is referred to as the trap-filled voltage  $V_{TFL}$ . Using  $V_{TFL}$ , the density of traps at  $E_t$  can be calculated from following relationship

$$N_t \approx \frac{3 \epsilon V_{TFL}}{2 q d^2}$$

where  $q$  is the electronic charge.

As may be seen in Fig. 2,  $j \propto V^2$  in region (b), and so the shallow-trap case is represented here; moreover, only one trap level is evident. The effective hole mobility at room temperature may be determined from Eq. (8), yielding  $\mu_{eff} = (1.58 \pm 0.55) \times 10^{-8} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . The temperature dependence of  $\mu_{eff}$  was measured from which the hole trap energy of  $\sim 0.1 \text{ eV}$  is obtained using Eq. (7). The hole trap density  $N_t$  can be determined from Eq. (9) using the experimental value of  $V_{TFL}$ . The value of  $V_{TFL}$  is  $\sim 2.2 \text{ eV}$ , then  $N_t$  can be estimated to be  $\sim 1.1 \times 10^{17} \text{ cm}^{-3}$ . Fig. 2 also gives the  $I(V)$  characteristics at decreasing voltage. From the slope of the  $\log I - \log V$  plot one observes that the current also depends quadratically on the voltage. Using Eq. (1) a hole mobility of  $(1.00 \pm 0.08) \times 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  is obtained; in this case we consider the hole to be the free carrier, justified below.

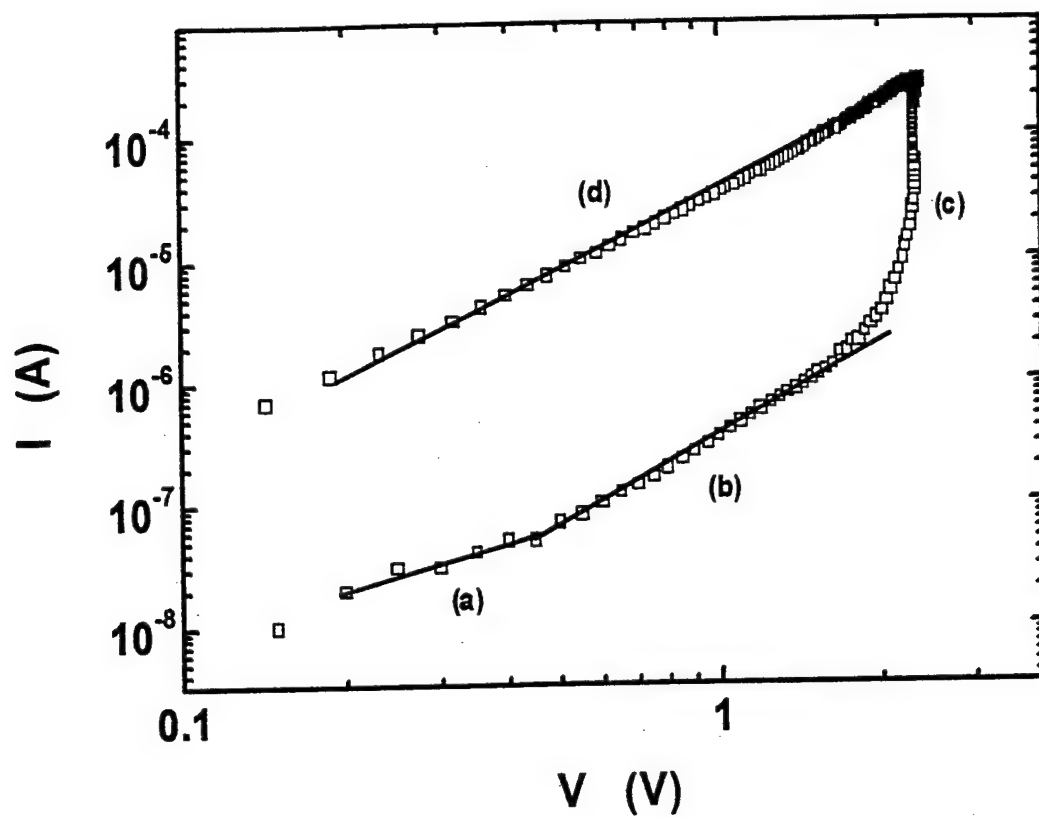


Figure 2

These experimental results clearly demonstrate that the electron current and hole current are space-charge limited with traps. By analyzing data from metal/polymer/metal sandwich devices, we have determined the hole mobility, hole trap energy and density, and electron characteristic energy and electron trap density.

## B. Blends (1, 2, 3, 10, 11, 19, 31, 34, 35, 38, 40)

### a) Copolymer Effects

There is continuous interest in understanding the principles governing the miscibility and phase domain formation for better controlling or predicting the phase behavior in multicomponent polymer systems. Simple models providing a useful framework for describing blends with controlled phase behavior have emerged, among which the Flory-Huggins equation and the empirical Flory-Huggins  $\chi$  models have been the most used.

It is known that miscibility in polymer blends is strongly dependent on the chain microstructure. Composition and sequence distribution in a copolymer, stereo-configuration, branching and crosslinking are structural features affecting local environments, whereas the size (molecular weight) and shape of molecules (chain flexibility) have long-range effects. The effect of molecular size on miscibility is clearly described -- with increasing molecular



weight, miscibility decreases. The combinatorial part in Flory-Huggins theory accounts for this effect. We have developed a mean-field theory of random copolymer blends based on the mixture of polymer segment concept. It was shown that using the mean-field approach, phase behavior of blends can be described by the pair interactions between all segments in the blends. This theory provided also a general explanation for the effect of chemical composition on miscibility. The model is reliable and a fast method for correlating experimental results and to describe the phase behavior of polymer blends. It has become widely used in description of miscibility/immiscibility phenomena.

The mean-field model has been comprehensively tested by using a data base involving blends of various polymer systems based mainly on styrene polymer derivatives and polymers on the basis of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Most of these experimental data have been obtained in our laboratory. Our computerized data base contains presently data for eighty binary polymer systems. Since new experimental data became available, it has been possible to revise some of the parameters based on limited information and to establish the "best fit values" for the segmental interaction parameters.

The study concentrated on the miscibility and phase behavior of polymer systems based on styrene polymer derivatives, PPO and partially sulfonylated PPO random copolymers (SPPO) which consist of sulfonylated and

unsulfonylated phenylene oxide units. Homopolymer-homopolymer, homopolymer-random copolymer systems, as well as blends of two random copolymers and alternating and random copolymers have been considered.

The polymer systems studied and the best fit  $\chi_{ij}$  are summarized in the Table.

The Flory-Huggins expression, based on a lattice theory, for the Gibbs energy of mixing for mixture of two polymers can be written:

$$\frac{\Delta G^M}{RT} = \underbrace{\frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2}_{\text{combinatorial term}} + \underbrace{\chi_{blend} \phi_1 \phi_2}_{\text{residual term}}$$

where  $N_1$  and  $N_2$  are the number of lattice cells occupied by polymer 1 and 2,  $\phi_1$  and  $\phi_2$  their volume fractions calculated on the basis of lattice occupancy, respectively, and  $\chi$  is a dimensionless overall interaction parameter for the polymer-polymer system. In practice, the  $\chi$  parameter exhibit considerable variation with temperature and composition. The combinatorial contribution of the expression to the Gibbs energy of mixing is due to the differences in size of molecules, and the residual contribution essentially due to the energetic interaction.

The mean-field theory provided the evaluation of  $\chi_{blend}$  parameter in a group contribution framework, in terms of segmental interactions, where segments are defined as monomer repeating units. In this model a polymer molecule is assumed to consist of number of segments, and a polymer blend is

a mixture of polymer segments. It is assumed that each segment occupies one lattice site. The excluded volume effect is taken into account by the requirement that a site can be occupied only once. The residual term assumes that the molecular segments are randomly mixed in the polymer mixture. The model neglects free volume contributions to the free energy of mixing and it does not take into account any possible specific interactions.

For the most general case of mixtures of two random copolymers of the type  $(A_{1-x}B_{xN_1}/(C_{1-y}D_y)_{N_2})$ , the overall interaction parameter  $\chi_{blend}$  can be expressed as a linear combination of the segmental interaction parameters,  $\chi_{ij}$ :

$$\begin{aligned}\chi_{blend} = & (1-x)(1-y)\chi_{AC} + (1-x)y\chi_{AD} + x(1-y)\chi_{BC} + xy\chi_{BD} \\ & - x(1-x)\chi_{AB} - y(1-y)\chi_{CD}\end{aligned}$$

where the definition of the respective  $\chi_{ij}$  parameters is obvious from their subscript, and comonomer compositions  $x$  and  $y$  should be expressed on the basis of lattice sites occupancy. The first four terms on the right-hand side of equation (2) define additive intermolecular interactions between the non-bonded component monomers in the mixture of two copolymers, weighted according to the copolymer compositions, whereas the remaining two terms define the intramolecular forces between the two different monomers comprising each of the copolymers.

In the present work the calculation employed volume fractions based on Bondi's van der Waals volumes which may be considered as the best expression of a lattice occupancy.

The criterion for miscibility of blends is that  $\chi_{blend}$  must be less than a critical value  $\chi_{blend}^{crit}$ , which for monodisperse polymers may be calculated on the basis of the number of lattice cells occupied:

$$\chi_{blend}^{crit} = 0.5 (N_1^{-0.5} + N_2^{-0.5})^2$$

where  $N_1$  and  $N_2$  are the number of lattice cells occupied by polymers 1 and 2.

The boundary between miscibility and immiscibility domains for copolymer/copolymer system where  $\chi_{blend} = \chi_{blend}^{crit}$  is described by a function expressed in terms of  $x$  and  $y$ , such that:

$$f(x,y) = \chi_{blend} - \chi_{blend}^{crit} = 0$$

In the present work the experimental data of eighty binary polymer blends have been selected for the estimation of the segmental interaction parameters. We have chosen to estimate the parameters that will minimize the following expression:

$$F = \sum_n \left( \frac{\chi_{blend,n} - \chi_{blend}^{crit}}{\chi_{blend}^{crit}} \right)^2$$

where the sum is extended to a set of points of coordinates  $x_n$  and  $y_n$  situated at the border miscibility-immiscibility, and  $\chi_{blend}^{crit}$  is calculated using equation (3). The conformational entropic term  $\chi_{blend}^{crit}$  is molecular weight related and calculated from the number of repeating units of respective blend components.

Due to the large number of repeating units,  $\chi_{\text{blend}}^{\text{crit}}$  are in range 0.002 to 0.006. The optimization algorithm used in the parameter estimation program is a modified Levenberg-Marquard algorithm.

In summarizing the results of our studies on the miscibility of mentioned polymer blends it is evident that a remarkable agreement for all systems studied exists between the miscibility-immiscibility boundaries obtained experimentally and by using the mean-field model with revised parameters. It is also evident that the interaction parameters derived and listed in the Table are sufficiently quantitative to be of predictive value of the copolymer systems studied in this work.

b) Polyvinyl butyral (PVB) (17, 37, 44)

Polyvinyl butyral is a macromolecule obtained by partial or full butyralisation of polyvinyl alcohol. In the former case, it may be regarded as a random copolymer formed by the butyral and the unreacted vinyl alcohol units. It is possible to obtain this copolymer over a wide range of compositions and thereby obtain systems in which one may systematically investigate (for example) the effects of hydrophilic/hydrophobic variations. We have started a study of the miscibility of PVB with a range of homo- and copolymers using for analysis the mean value treatment discussed above. It appears that a wide range of miscibility/compatibility phenomena can be accessed, with a corresponding range of physical properties of the blend systems.

### C. Dynamic Light Scattering (21, 29, 32)

Dynamic light scattering (photon correlation spectroscopy) has been used in these laboratories for many years to study solution behavior of polymers. In the period of this grant, we have investigated the key problem of chain collapse below the  $\Theta$ -point. For example we have considered the coil-to-globule transition behavior of atactic and syndiotactic poly(methyl methacrylates), PMMA, in the theta solvent, n-butyl chloride (nBuCl). Changes in  $R_h$  in these polymers with temperature in dilute theta solutions were investigated. The hydrodynamic size of atactic PMMA (a-PMMA-1) in nBuCl ( $M_w$ :  $2.55 \times 10^6$  g/mol) decreases to 61% of that in the unperturbed state at 13.0°C. Another sample, atactic PMMA (a-PMMA-2) with higher molecular weight ( $M_w$ :  $3.3 \times 10^6$  g/mol) shows higher contraction in the same theta solvent ( $\alpha_\eta = R_h(T) / R_h(\theta) = 0.44$  at a lower temperature, 7.25°C. Although syndiotactic PMMA (s-PMMA) has lower molecular weight than that of atactic samples ( $M_w$ :  $1.2 \times 10^6$ ), a comparable chain collapse was observed ( $\alpha_\eta = 0.63$ ) at 9.0°C.

It is well known that syndiotactic PMMA forms stereocomplexes and self-aggregates in several solvents. However in this work we used highly dilute solutions ( $\sim 10^{-5}$  g/ml) and we did not observe aggregation which was specific to the stereoregularity. Finally, our results showed that even in the mostly collapsed globule, the estimated volume fraction in polymer domain,  $\phi$  is between 0.09 and 0.22. This implies that the chain contains a large amount of solvent (n-butyl chloride, 78-91%) even in the globule state.

#### D. Other Studies

We have continued investigations of the structures of doped conducting polymers (8, 25, 32) and of the photophysics of stilbene derivatives (22). All the above results are detailed in the 48 publications cited.

Table 1. Segmental interaction parameters at 473K

Segment pair	$\chi_{ij}$	Segment pair	$\chi_{ij}$
S,PO	-0.043	SPO,pFS	0.046
S,SPO	0.22	SPO,oClS	0.175
S,oFS	0.0025	SPO,pClS	0.009
S,pFS	0.06	SPO,oBrS	0.15
S,oClS	0.005	SPO,pBrS	0.01
S,pClS	0.055	SPO,oMS	0.18
S,oBrS	0.013	SPO,pMS	0.17
S,pBrS	0.048	SPO,AMS	0.505
S,pIS	0.09	SPO,MAN	0.81
S,oMS	0.0025	SPO,PhMI	0.39
S,pMS	0.003	SPO,AN	0.20
S,MAN	1.85	oFS,pFS	0.04
S,PhMI	0.29	oFS,oClS	0.064
S,AN	0.98	oFS,pClS	0.07
S,MMA	0.04	oFS,oBrS	0.042
PO,SPO	0.25	oFS,pBrS	0.108
PO,oFS	0.005	pFS,oClS	0.11
PO,pFS	0.057	pFS,pClS	0.043
PO,oClS	0.021	pFS,oBrS	0.12
PO,pClS	0.034	pFS,pBrS	0.11
PO,oBrS	0.047	oClS,pClS	0.09
PO,pBrS	0.055	oBrS,pBrS	0.10
PO,pIS	0.097	oMS,pMS	0.01
PO,oMS	0.006	pMS,AN	0.91
PO,pMS	0.005	AMS,MAN	0.152
PO,AMS	0.11	AMS,PhMI	1.22
PO,MAN	1.68	MMA,AN	0.50
PO,PhMI	0.90	MMA,MAN	1.20
PO,AN	1.23	AN,MAN	0.04
PO,MMA	0.21	AN,PhMI	0.07
SPO,oFS	0.176		



AN	=	acrylonitrile
BrPPO	=	brominated poly(2,6-dimethyl-1,4-phenylene oxide)
MAN	=	maleic anhydride
MI	=	maleimide
MMA	=	methyl methacrylate
MMI	=	methyl maleimide
MS	=	methylstyrene
PhMI	=	phenyl maleimide
PAMS	=	poly( $\alpha$ -methylstyrene)
PmClS	=	poly(m-chlorostyrene)
PmMS	=	poly(m-methylstyrene)
PO	=	2,6-dimethyl-1,4-phenylene oxide
PoBrS	=	poly(o-bromostyrene)
PoClS	=	poly(o-chlorostyrene)
PoFS	=	poly(o-fluorostyrene)
PoMS	=	poly(o-methylstyrene)
PpBrS	=	poly(p-bromostyrene)
PpClS	=	poly(p-chlorostyrene)
PpFS	=	poly(p-fluorostyrene)
PpIS	=	poly(p-iodostyrene)
PpMS	=	poly(p-methylstyrene)
PPO	=	poly(2,6-dimethyl-1,4-phenylene oxide)
PS	=	polystyrene
S	=	styrene
SPO	=	sulfonylated 2,6-dimethyl-1,4-phenylene oxide
SPPO	=	sulfonylated poly(2,6-dimethyl-1,4-phenylene oxide)
P(AMS&MAN)	=	poly( $\alpha$ -methylstyrene-co-maleic anhydride)
P(AMS&MMI)	=	poly( $\alpha$ -methylstyrene-co-methyl maleimide)
P(AMS&PhMI)	=	poly( $\alpha$ -methylstyrene-co-phenyl maleimide)
P(MMA&AN)	=	poly(methyl methacrylate-co-acrylonitrile)
P(MMA&BMA)	=	poly(methyl methacrylate-co-n-butyl methacrylate)
P(MMA&MAN)	=	poly(methyl methacrylate-co-maleic anhydride)
P(oBrS&pBrS)	=	poly(o-bromostyrene-co-p-bromostyrene)
P(oClS&pClS)	=	poly(o-chlorostyrene-co-p-chlorostyrene)

P(oFS&oBrS)	=	poly(o-fluorostyrene-co-o-bromostyrene)
P(oFS&oClS)	=	poly(o-fluorostyrene-co-o-chlorostyrene)
P(oFS&pBrS)	=	poly(o-fluorostyrene-co-p-bromostyrene)
P(oFS&pClS)	=	poly(o-fluorostyrene-co-p-chlorostyrene)
P(oFS&pFS)	=	poly(o-fluorostyrene-co-p-fluorostyrene)
P(oMS&pMS)	=	poly(o-methylstyrene-co-p-methylstyrene)
P(pFS&oBrS)	=	poly(p-fluorostyrene-co-o-bromostyrene)
P(pFS&oClS)	=	poly(p-fluorostyrene-co-o-chlorostyrene)
P(pFS&pBrS)	=	poly(p-fluorostyrene-co-p-bromostyrene)
P(pFS&pClS)	=	poly(p-fluorostyrene-co-p-chlorostyrene)
P(PhVBE&PhMI)	=	poly(phenylvinyl sec-butyl ether-co-phenyl maleimide)
P(PhVEE&PhMI)	=	poly(phenylvinyl ethyl ether-co-phenyl maleimide)
P(S&AMS)	=	poly(styrene-co- $\alpha$ -methylstyrene)
P(S&AMS)	=	poly(styrene-co- $\alpha$ -methylstyrene)
P(S&AN)	=	poly(styrene-co-acrylonitrile)
P(S&MAN)	=	poly(styrene-co-maleic anhydride)
P(S&MMA)	=	poly(styrene-co-methyl methacrylate)
P(S&oBrS)	=	poly(styrene-co-o-bromostyrene)
P(S&oClS)	=	poly(styrene-co-o-chlorostyrene)
P(S&oFS)	=	poly(styrene-co-o-fluorostyrene)
P(S&oMS)	=	poly(styrene-co-o-methylstyrene)
P(S&pBrS)	=	poly(styrene-co-p-bromostyrene)
P(S&pClS)	=	poly(styrene-co-p-chlorostyrene)
P(S&pFS)	=	poly(styrene-co-p-fluorostyrene)
P(S&PhMI)	=	poly(styrene-co-phenylmaleimide)
P(S&pMS)	=	poly(styrene-co-p-methylstyrene)

# VIII. PUBLICATIONS IN PERIOD WITH AFOSR SUPPORT

Forty-eight scientific papers (31 Published, 17 in press) were completed with full or partial AFOSR support during the grant period.

1. *Thermochimica Acta*, 275, 259-268 (1996) (with R. Vukovic, G. Bogdanic, A. Erceg, D. Fles and W.J. MacKnight) "Copolymer Blends of Phenylsulphonylated Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly(*p*-fluorostyrene-co-*p*(*o*)-chlorostyrene)".
2. *Thermochimica Acta*, 282/283, 399-410 (1996) (with S. Djadoun and A.S.H. Hamou) "Blends of Poly(isobutyl methacrylate) with Poly(styrene-co-acrylic acid) with Poly(styrene-co-*N,N*-dimethyl aminoethyl methacrylate)".
3. *Thermochimica Acta*, 285, 141-154 (1996) (with R. Vukovic, G. Bogdanic, A. Erceg, D. Fles and W.J. MacKnight) "Miscibility and Phase Separation Study of Blends of Random Copolymers of Poly[*ortho*(*para*)-fluorostyrene-co-*ortho*(*para*)-bromostyrene] with Phenylsulphonylated Poly(2,6-dimethyl-1,4-phenylene oxide) Copolymers by Thermal Methods".
4. *Polymer Bulletin*, 38, 347-351 (1997) (with R. Vukovic, D. Fles, I. Smit and A. Waddon) "Smectic Ordering in Poly(4-maleimidocholesterylbenzoate), Poly(6-maleimidocholesteryl-hexanoate) and Alternating Copolymers with Styrene,  $\alpha$ - and  $\beta$ -methylstyrene and Phenylvinyl Ethyl Ether".
5. *Turkish J. of Chem.*, 21, 1-5 (1997) (with B. Hu and Z. Yang) "Polymer Light Emitting Diodes".
6. *Polym. Bull.*, 39, 93-99 (1997) (with E. Fekete, Z. Peredy, E. Földes and B. Pukánszky) "Effect of Specific Interactions on Film Casting of High Temperature Polymers".
7. *Appl. Phys. Lett.*, 71, 999-1001 (1997) (with N. Kumar, J. Bhawalkar, P. Prasad and B. Hu) "Solid-state Tunable Cavity Lasing in a Poly(Para-phenylene Vinylene) Derivative Alternating Block Co-polymer".
8. *Synthetic Metals*, 90, 5-11 (1997) (with D. Gonçalves, D.S. dos Santos, Jr., L.H.C. Mattoso, L. Akcelrud and R.M. Faria) "Poly(*o*-methoxyaniline): Solubility, Deprotonation-Protonation Process in Solution and Cast Films".
9. *Macromol. Symp.*, 124, 83-87 (1997) (with Z. Yang and B. Hu) "Electroluminescence in Polymers".

10. Fluid Phase Equil., 139, 277-294 (1997) (with G. Bogdanic, R. Vukovic and W.J. MacKnight) "Estimation of the Segmental Interaction Parameters of Polymer Blends Containing Styrene and Poly(2,6-dimethyl-1,4-phenylene oxide) Derivatives".
11. Thermochim. Acta, 306, 135-141 (1997) (with R. Vukovic, G. Bogdanic, A. Erceg, D. Flex and W.J. MacKnight) "Miscibility-Immiscibility Behavior in Blends of Phenylsulfonylated Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly[styrene-co-ortho(para)-chlorostyrene]".
12. Macromolecules, 30, 8286-8292 (1997) (with R.M. Gurge, A.M. Sarker P.M. Lahti and B. Hu) "Light Emitting Properties of Fluorine-Substituted Poly(1,4-phenylene vinylenes)".
13. Synthetic Metals, 90, 73-76 (1997) (with E. Etteedgui, G.T. Davis and B.Hu) "Degradation of Polymer-based Light-emitting Diodes During Operation".
14. Polimeri, 18, 158-162 (1997) "Elektroluminiscencija Polimera".
15. Synthetic Metals, 92, 157-160 (1998) (with B. Hu) "Comparison of Electroluminescent Quantum Efficiencies of PPV and a PPV-related Alternating Block Copolymer".
16. J. Macromol. Sci., Part A: Pure and Applied Chemistry, 35, 233-247 (1998) (with Z. Yang and B. Hu) "Contributions of Nonconjugated Spacers to Properties of Electroluminescent Block Copolymers".
17. Turkish J. of Chem., 21, 229-238 (1997) (with Z.M. Zhou, D.J. David and W.J. MacKnight) "Synthesis Characterization and Miscibility of Polyvinyl Butyrals of Varying Vinyl Alcohol Contents".
18. Chemical Physics, 227, 263-270 (1998) (with B. Hu) "Interfacial Effects in Polymer LEDs".
19. Polymer, 39, 2847-2850 (1998) (with R. Vuković, G. Bogdanić, A. Erceg, D. Fleš and W.J. MacKnight) "Phase Behaviour in Blends of Poly[styrene-co-ortho(para)-bromostyrene] and Phenylsulfonylated poly(2,6-dimethyl-1,4-phenylene oxide) Copolymers".
20. J. Appl. Phys., 83, 6002-6006 (1998) (with B. Hu and N. Zhang) "Bright Red Electroluminescence from a Dye/Copolymer Blend".

21. Polymer, 39, 3657-3663 (1998) (with E.E. Hamurcu, L. Akcelrud and B.M. Baysal) "Dynamic Light Scattering Studies of Poly(4-chlorostyrene) and Poly(2-chlorostyrene) in Theta Solvents".
22. Macromol. Chem.Phys., 199, 1255-1261 (1998) (with M. Aguiar, B. Hu and L. Akcelrud) "Fluorescent Dimer Formation in Stilbene-derived Chromophoric Polymers".
23. Polym. Adv. Technol., 9, 504-510 (1998) (with R.M. Gurge, M. Hickl, G. Krause, P.M. Lahti, B. Hu and Z. Yang) "Synthesis of a Green-emitting Alternating Block Copolymer".
24. Macromolecules, 31, 6730-6732 (1998) (with Y. Pang, J. Li and B. Hu) "A Processible Poly(phenylene ethynylene) with Strong Photoluminescence: Synthesis and Characterization of Poly[*m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)]".
25. Phys. Rev. B, 58, 4089-4094 (1998) (with G. Mao and M.J. Winokur) "Formation of Layer Structures in H<sub>2</sub>SO<sub>4</sub> Intercalated Poly(*p*-phenylene vinylene)".
26. Xjenza, 3, 29-31 (1998) "A New Plastic Light Source: Electroluminescence".
27. Macromolecules, 32, 3946 (1999) (with Y. Pang, J. Li and B. Hu) "A Highly Luminescent Poly[*m*-phenylene vinylene)-*alt*(*p*-phenylene vinylene)] with Defined Conjugation Length and Improved Solubility".
28. J. Mol. Liq. 80, 179-205 (1999) (with V.J. McBrierty and S.J. Martin)"Understanding Hydrated Polymers: The Perspective of NMR".
29. J. Polym. Sci: Part B.: Polymer Physics, 37 2253-2260 (1999) (with E.E. Gürel, N. Kayaman and B.M. Baysal) "Dynamic Light Scattering Studies of Atactic and Syndiotactic Poly(methyl Methacrylate)s in Dilute Theta Solution".
30. J. Appl. Physics, 86, 6, 3181-3186, (1999) (with M. Dongge, I.A. Hümmelgen and B. Hu) "Charge Carrier Mobility in Electroluminescent Alternating Block Copolymers".
31. J. Phys. and Chem. Ref. Data, 28, 3, 851-868 (with R. Vukovic, G. Bogdanic and W.J. MacKnight) "Phase Behavior and Miscibility in Binary Blends Containing Polymers and Copolymers of Styrene, of 2,6-Dimethyl-1,4-Phenylene Oxide, and of Their Derivatives".

32. Phys. Rev. Letters: "The Generalized Anisotropic Planar Rotor Model and its Application to Polymer Intercalation Compounds". (Mao/Chen/Winokur) (in press)
33. Polymer: "Light-Emitting Copolymers of Cyano-Containing PPV-Based Chromophores and a Flexible Spacer" (Pinto/Hu/Akcelrud) (in press)
34. J. Appl. Polym. Sci.: "Atactic Poly(Methyl Methacrylate) Blended with Poly(3-D(-)Hydroxybutyrate): Miscibility and Mechanical Properties" (Cimmino/Iodice/Martuscelli/Silvestre) (in press)
35. Polymer: "Interaction, Miscibility and Phase Inversion in PBI/PI Blends" (Foldes/Fekete/Pukanszky) (in press)
36. Polymer: "Coil to Globule Transition Behaviour of Poly(Methyl Methacrylate) in Isoamyl Acetate" (Kayaman/Gürel/Baysal) (in press)
37. Polymer: "Miscibility of Polyvinyl Butyral/Nylon 6 Blends" (Jeong/Rooney/David/MacKnight/Kajiyama) (in press)
38. Proceedings of Meeting in Crete: "Microstructure and Copolymer Miscibility and Compatibility" (in press)
39. Phys. Rev. B: "Electron and Hole Transport in a Green-emitting Alternating Block Copolymer: Space-charge Limited Conduction with Traps" (Hummelgen/Ma/Hu) (in press)
40. J. Thermal Analysis and Calorimetry: "Miscibility of Some Polycarbonates with Polyvinyl Chloride and Chlorinated Polyvinyl Chloride". (Neill) (in press)
41. Polymer: "Selective Plasticization in Electroluminescent Block Copolymers" (Gürel/Pasco) (in press)
42. Proceedings of the Second Yugoslav Conference on Advanced Materials: "Light Emission from Macromolecules" (in press)
43. Macromolecules: "Kinetics of Coil-Globule Collapse in Poly(Methacrylate) in Dilute Theta Solutions" (Kayaman/Gürel/Baysal) (in press)
44. Polymer: "Miscibility and Characterization of Polyvinyl Butyral in Ternary Crystalline Systems: Polyvinyl Butyral/Polyvinyl Alcohol/Nylon 6 and Polyvinyl Butyral/Polymethyl Methacrylate" (Jeong/Rooney/David/MacKnight/Kajiyama) (in press)

45. Solid State Communications: "Determination of Electron Mobility in a Blue-Emitting Alternating Block Copolymer by Space-Charge-Limited Current Measurements" (Ma/Hümmelgen/Hu/Jing/L. Wang/F. Wang) (in press)
46. Macromolecules: "Synthesis of Substituted Poly(*p*-phenylenevinylene) Copolymers by the Heck Method for Luminescence Studies" (Pasco/Lahti) (in press)
47. J. Phys. D.: Appl. Phys.: "Charge Transport in a Blue-emitting Alternating Block Copolymer with a Small Spacer to Conjugated Segment Length Ratio" (Ma/Hümmelgen/Jing/Hong/L. Wang/Zhao/F. Wang) (in press)
48. Polymer: "Emitting Polymers Containing Cyano Groups. Synthesis and Photophysical Properties of a Fully Conjugated Polymer Obtained by Wittig Reaction" (Pinto/Hu/Akcelrud) (in press)